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Concerning the Reaction of 2-(10-Diazo-10*H*-anthracen-9-ylidene)-malonodinitrile and Related Compounds with the Cryptohydride System Formic Acid–Triethylamine

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Summary. The reaction of 2-(10-diazo-10*H*-anthracen-9-ylidene)-malonodinitrile (**1**) with the cryptohydride system formic acid – triethylamine was studied. The reaction product turned out to be anthracen-9-yl-acetonitrile (**2a**) instead of the expected 10-dicyanomethyl-9,10-dihydro-anthracene-9-yl formate. Compounds related to **1** yielded in this reaction the corresponding 10-substituted anthracen-9-yl-acetonitriles. A mechanism of this reaction is proposed. The product of the formic acid promoted decomposition of **1**, compound **3b**, as well as its tautomer **4b** were also obtained.

Keywords. Cryptohydride system formic acid – triethylamine; 2-(10-Diazo-10*H*-anthracene-9-ylidene)-malonodinitrile; 10-Substituted anthracen-9-yl-acetonitriles; 10-Substituted dicyanomethyl-anthracen-9-yl formates; Tautomerization; Synthesis.

Zur Reaktion von 2-(10-Diazo-10*H*-anthracen-9-yliden)-malodinitril und Verwandten Verbindungen mit dem Kryptohydridsystem Ameisensäure – Triethylamin

Zusammenfassung. Die Reaktion von 2-(10-Diazo-10*H*-anthracen-9-yliden)-malodinitril (**1**) mit dem Kryptohydridsystem Ameisensäure – Triethylamin wurde untersucht. Das Umsetzungsprodukt stellte sich als Anthracen-9-yl-acetonitril (**2a**) und nicht als erwartetes 10-Dicyanomethyl-9,10-dihydro-anthracen-9-yl-format heraus. Verwandte Verbindungen reagierten in dieser Reaktion zu 10-substituierten Anthracen-9-yl-acetonitrilen. Ein Mechanismus für diese Reaktion wird vorschlagen. Das Produkt der durch Ameisensäure initiierten Zersetzung von **1**, Verbindung **3b**, wie auch sein Tautomer **4b**, wurden ebenfalls dargestellt.

Introduction

2-(10-Diazo-10*H*-anthracen-9-ylidene)-malonodinitrile (**1**) has been shown to be a convenient starting material in the synthesis of 9,10-disubstituted 9,10-dihydro-anthracenes and 9,10-disubstituted anthracenes [1]. To expand the synthetic utility of this compound by transforming its functionalities, we tested its reactivity towards a cryptohydride system, the azeotropic mixture of formic acid – triethylamine in dimethylformamide solution [2]. This reagent has been specifically developed for the reduction of the C=C fragments in ylidene malononitriles and related

compounds. The idea was to develop a one-pot procedure consisting of the formic acid promoted decomposition of the diazo group [3] and reduction of the dicyanomethylene moiety. This procedure was supposed to yield 10-dicyanomethyl-9,10-dihydroanthracen-9-yl formate as the product.

Results and Discussion

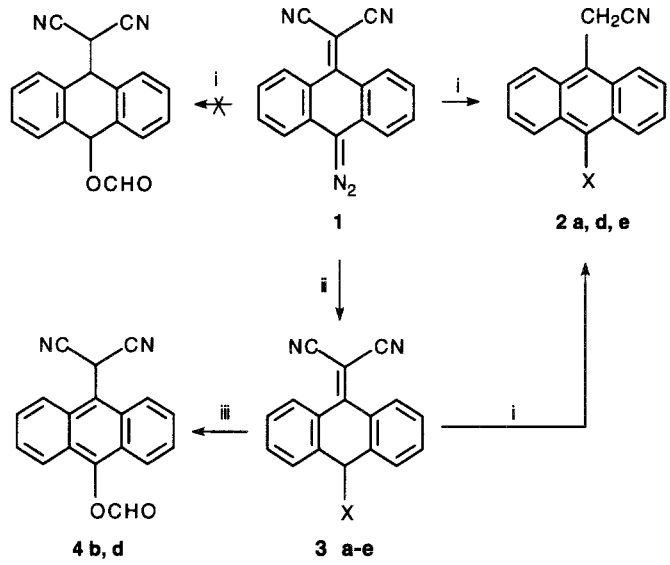
Proceeding according to the introduction resulted in no reaction at all. Increasing the reaction time to more than 20 hours, or refluxing the mixture for 3 hours, resulted in a color change from cherry-red to yellow and yielded a product with at least two by-products accompanied by partial resinification. However, the result was improved when the reaction was carried out without using dimethylformamide as the solvent, *i.e.*, in the mixture formic acid – triethyl amine. Heating and short refluxing gave rise to a vigorous gas evolution and a color change. The exclusive reaction product could be identified as anthracen-9-yl-acetonitrile (**2a**) which had been previously obtained *via* the *Beckmann* rearrangement of 9,10-dihydro-9,10-(11-oxo-ethano)-anthracene oxime [4].

To explain this reaction course it was proposed that the intermediate in this reaction could be 10-dicyanomethylene-9,10-dihydro-anthracen-9-yl formate (**3b**), the product of the initial formic acid decomposition of **1** [3]. To test this hypothesis, we subjected **1** to the action of formic acid which produced **3b**. However, the reaction of **3b** with formic acid – triethylamine produced a mixture of unidentified products with only a trace amount of **2a**. Under basic conditions, **3b** smoothly tautomerized into **4b** in analogy to the observations reported in Ref. [1].

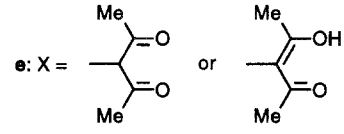
For a further screening, compounds related to **1** were tested which in principle should be able to react with the formic acid – triethylamine system. Thus, (10-dicyanomethylene-9,10-dihydroanthracen-9-yl-mercapto)-acetic acid ethyl ester (**3c**) quantitatively produced **2a**, 2-(10-methoxy-10*H*-anthracen-9-ylidene)-malonodinitrile (**3d**) afforded **2d**, and 2-(10-(1-acetyl-2-oxo-propen)-10*H*-anthracen-9-ylidene)-malonodinitrile (**3e**) yielded **2e**.

These results could be rationalized as follows. First, compounds **3** were deprotonated to form anions **5** (the transformation of **1** and **3c** into **2a** obviously proceeds *via* **3a**). This was indicated by the appearance of a red color of the reaction mixtures [1]. Second, disappearance of this red color upon heating pointed to the "aromatization" of **5** which upon subsequent protonation yielded **4**. The latter produced **2** by means of a cryptohydride transfer from the formiate ion accompanied by carbon dioxide evolution. To corroborate this hypothesis, 2-(10-methoxy-anthracen-9-yl)-malonodinitrile (**4d**) [1] was also tested as a substrate for the reaction. The main product of this reaction was indeed found to be **2d**.

The constitution of compounds **2a**, **2d**, **2e**, **3b**, and **4b** was derived from their spectroscopic data. Thus, the mass spectra contained the appropriate molecular ion peaks. The ^{1}H NMR spectra of **2a**, **2d**, and **2e** contained – in addition to the aromatic proton multiplet signals displaying a splitting pattern of 2H:2H:4H – a singlet of the methylene group at 4.57–4.68 ppm. In the spectrum of **2a**, a singlet at 8.53 ppm (10-H) and in the spectrum of **2d** a singlet at 4.16 ppm (methyl group) were also present. Compound **2e** (in contrast to its precursor diketone **3e** [1]) could be assigned as an enol form according to its ^{1}H NMR spectrum. It displayed a signal at low frequency (17.10 ppm; OH) and two singlets of methyl groups at 1.62 and 1.61 ppm.

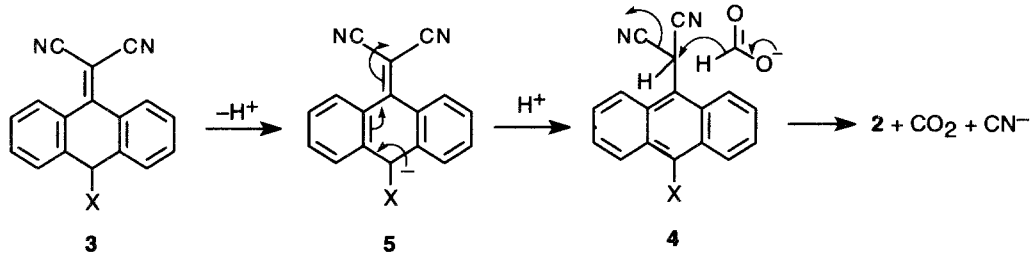


a: X = H; **b**: X = OCHO; **c**: X = SCH_2CO_2Et; **d**: X = OMe;



i = HCOOH - Et_3N; ii = HX - H_2SO_4 or HX; iii = 1. Et_3N, 2. HCl;

Scheme 1



Scheme 2

The ^1H NMR spectrum of **3b** and its tautomer **4b** were found to be significantly different (see also data in Ref. [1]): the signal of the CH-proton in the spectrum of **3b** was observed at 6.95 ppm, whereas the signal of the CH-proton in the spectrum of **4b** was found at 6.39 ppm. The latter spectrum also contained a signal of the formyl proton at 8.74 ppm, whereas in the spectrum of **3b** this signal was overlapped by aromatic proton signals. This resulted in two multiplets with relative intensities 2H:7H. It should be noted that the aromatic protons in the NMR spectrum of **4b** exhibited the same intensity pattern (2H:2H:4H) as the aromatic protons in the spectra of **2a**, **2d**, and **2e**.

In the ^{13}C NMR spectra of compounds **2a**, **2d**, and **2e**, the characteristic signals of cyano groups at 117.8–117.0 ppm and CH_2 signals at 15.4–16.5 ppm were observed along with the aromatic carbon

signals. The remaining signals in these spectra (cf. Experimental) supported the proposed structures. The ^{13}C NMR spectra of the formates **3b** and **4b** (Experimental) were found to be similar to the spectra of homologous acetates and propionates [1] and thus unambiguously confirmed their structures.

The IR spectra of compounds **2a**, **2d**, and **2e** contained characteristic bands of nitrile groups at 2241–2249 cm^{-1}. In the spectrum of **3b**, the conjugated nitrile group vibrations were present at 2223 cm^{-1}, whereas in the spectrum of its aromatic tautomer this band was not observed at all. The intensive bands of the carbonyl groups – a broad band at 1621 and bands at 1731 and 1760 cm^{-1} (in the spectra of **2e**, **3b**, and **4b**) – were also in agreement with the proposed structures.

The electronic spectra of **2a**, **2d**, and **2e** displayed absorption bands typical of anthracenes. Thus, very intensive bands were observed at 253–259 nm with ε values of 133000–167000. Much less intensive bands (ε = 12000–15000) at 216–219 nm as well as weak vibronic progression bands in the 260–400 nm region were also observed. The UV spectrum of the partially "nonaromatic" **3b** consisted of three intensive bands at 310, 252, and 202 nm and was similar to the related compounds described in Ref. [1]. The absorption spectrum of **4b** also displayed the characteristic vibronic progression bands of anthracenes and was similar to the spectra of **2a**, **2d**, and **2e** (Experimental). In addition, **4b** showed a weak band in the visible region at 473 nm.

Fluoresence spectra of anthracenes **2a**, **2d**, **2e**, and **4b** were also measured. The irradiation of the corresponding solutions (excitation wavelength 342 nm) produced a blue fluorescence. Depending on the structures, the spectra contained different numbers of absorption bands; the quantum yield values were also different. Thus, in the spectrum of **4b**, only one maximum at 380 nm [1] was observed with a quantum yield of only 0.02. In contrast to this dicyanomethyl derivative, the spectra of **2a** and **2e** were similar to the fluorescence spectrum of anthracene (see Experimental) with quantum yields of 0.20 and 0.36. However, the fluorescence spectrum of **2d** did not show the anthracene characteristics, and the quantum yield of 0.06 turned out to be also rather low.

Experimental

Melting points were measured on a Kofler hot stage microscope (Reichert, Vienna) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded by means of a Bruker AC-200 spectrometer. IR spectra were obtained on a Biorad-FT-IR-45-instrument. The UV/Vis spectra were measured by means of a Hitachi U-3210-spectrophotometer. The fluorescence spectra were recorded using a Hitachi-F-4010 spectrofluorimeter. As the standard for quantum yield determinations, anthracene (quantum yield Φ_f = 0.40 [5]) was used. The mass spectra were recorded on a Hewlett Packard 5989A MS instrument (70 eV, direct probe inlet) at 80–140 °C, depending on the melting points of the compounds. **1** was prepared as previously described [1].

Anthracen-9-yl-acetonitrile (**2a**; $C_{16}H_{11}N$)

A suspension of 60 mg of **1**, or 80 mg of **2c**, (0.22 mmol) in 5 ml of the azeotropic mixture HCOOH-Et_3N (*i.e.* 5:2 molar ≈ 2:3 volume ratio) was heated to reflux for 2 min and then stirred without heating for additional 5 min. After cooling to room temperature, the resulting yellow solution was quenched with 100 ml water and the precipitate formed was isolated and dried. Yield: 48 mg (98%); m.p.: 161–163 °C (methanol; lit. m.p.: 161–163 °C (ethyl acetate) [4]); ^1H NMR ($CDCl_3$, δ, 200 MHz): 8.53 (s, 10-H), 8.20–8.16 (m, $2H_{arom}$), 8.10–8.05 (m, $2H_{arom}$), 7.69–7.50 (m, $4H_{arom}$), 4.61 (s, CH_2CN) ppm; ^{13}C NMR ($CDCl_3$, δ, 50 MHz): 130.6, 129.0, 128.7, 128.1, 126.5, 124.5, 122.2, 119.4 (C_{arom}), 117.0 (CN), 15.4 (CH_2) ppm; IR (KBr): ν = 3053, 2937, 2241, 1623 cm^{-1}; UV (ethanol): λ_{max} = 385 (8600), 365 (9300), 347 (6200), 332 (3200), 253 (166700), 219 (12600) nm (ε); Fluorescence (ethanol): λ = 391 (0.9), 414 (1.0), 438 (0.5) nm (relative intensity), Φ_f = 0.20; MS: *m/e* (%) = 217 (M^+, 100), 189 (21), 176 (5), 108 (11), 94 (16).

10-Methoxy-anthracen-9-yl-acetonitrile (**2d**; $C_{17}H_{13}NO$)

2d was obtained starting from **3d** [1] using the procedure described above for **2a** in 94% yield. M.p.: 168–170 °C (methanol); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 8.43–8.38 (m, $2H_{arom}$). 8.20–8.15 (m, $2H_{arom}$), 7.70–7.53 (m, $4H_{arom}$), 4.57 (s, CH_2CN), 4.16 (s, CH_3) ppm; ^{13}C NMR ($CDCl_3$, δ, 50 MHz): 153.8 (C-10), 130.6, 127.4, 125.2, 124.4, 123.4, 123.3 (C_{arom}), 117.8 (CN), 116.5 (C-9), 63.6 (OCH_3), 16.1 (CH_2) ppm; IR(KBr): $\nu = 2937$, 2245, 1620 cm^{-1}; UV (ethanol): $\lambda_{max} = 398$ (7100), 377 (8500), 358 (5700), 259 (146700), 219 (12800) nm (ε); Fluorescence (ethanol): $\lambda = 380$ (1), 432 (0.6) nm (relative intensity), $\Phi_f = 0.06$; MS: *m/e* (%) = 247 (M^+, 51), 232 (100), 204 (21), 176 (31), 88 (31), 57 (31), 43 (85).

(10-(1-Acetyl-2-hydroxy-propenyl)-anthracen-9-yl)-acetonitrile (**2e**; $C_{21}H_{17}NO_2$)

2e was obtained starting from **3e** [1] using the procedure described above for **2a** in 94% yield. M.p.: 191–194 °C (methanol); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 17.10 (s, OH), 8.28–8.24 (m, $2H_{arom}$), 8.11–8.06 (m, $2H_{arom}$), 7.74–7.55 (m, $4H_{arom}$), 4.68 (s, CH_2CN), 1.62 (s, CH_3), 1.61 (s, CH_3) ppm; ^{13}C NMR ($CDCl_3$, δ, 50 MHz): 192.0 (CO), 132.5, 131.1, 129.9, 127.3, 126.5, 123.7, 122.0 (due to an overlap, only 7 signals instead of 8 of C_{arom} could be observed), 117.6 (CN), 109.2 (MeCO–**C**=C(OH)Me), 23.8 (CH_3), 16.5 (CH_2) ppm; IR (KBr): $\nu = 3070$, 3045, 2249, 1621 (broad) cm^{-1}; UV (ethanol): $\lambda_{max} = 394$ (12900), 374 (12500), 355 (7500), 338 (3900), 280 (9700), 257 (133400), 216 (14700) nm (ε); Fluorescence (ethanol): $\lambda = 380$ (0.1), 402 (1.0), 424 (1.0), 448 (0.4) nm (relative intensity), $\Phi_f = 0.36$; MS: *m/e* (%) = 315 (M^+, 48), 272 (21), 255 (8), 231 (10), 202 (13), 43 (100).

10-Dicyanomethylene-9,10-dihydro-anthracen-9-yl formate (**3b**; $C_{18}H_{10}N_2O_2$)

A mixture of 120 mg **1** (0.448 mmol) and 15 ml HCOOH was refluxed for 15 min and then poured into 100 ml water. The forming precipitate was isolated, dried, and chromatographed on a silicagel (60–200 mesh) column, eluent $CHCl_3/CH_3OH$ (40:1). Yield: 65 mg (47%); m.p.: 166–182 °C (slow dec.); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 8.17–8.10 (m, $2H_{arom}$), 7.71–7.51 (m, $6H_{arom}$ + CHO), 6.95 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 50 MHz): 163.4 (C-10), 160.1 (CO), 134.4, 132.7, 132.3, 129.4, 129.3, 127.4 ($6C_{arom}$), 113.8 (2CN), 81.0 (=**C**$(CN)_2$), 69.9 (C-9) ppm; IR (KBr): $\nu = 2889$, 2223, 1731, 1591 cm^{-1}; UV (ethanol): $\lambda_{max} = 310$ (16500), 252 (24000), 202 (30400) nm (ε); MS: *m/e* (%) = 286 (M^+, 19), 256 (65), 241 (100), 228 (42), 214 (39), 193 (95), 165 (34), 150 (6), 111 (13), 87 (43), 83 (48), 43 (51).

10-Dicyanomethyl-anthracen-9-yl formate (**4b**; $C_{18}H_{10}N_2O_2$)

To a stirred solution of 72 mg of **3b** (0.25 mmol) in 10 ml tetrahydrofuran at room temperature 0.1 ml triethylamine were added. The mixture was stirred for 5 min, quenched with 1 ml conc. HCl in 10 ml water, and extracted with CH_2Cl_2. The extract was washed with water, dried over $MgSO_4$ and evaporated to give 66 mg (92%) of **4b**. M.p.: 183–200 °C (ethyl acetate, slow dec.); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 8.74 (s, CHO), 8.33–8.28 (m, $2H_{arom}$), 8.18–8.14 (m, $2H_{arom}$), 7.85–7.64 (m, $4H_{arom}$), 6.39 (s, CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 50 MHz): 158.7 (CO), 144.7 (C-9), 129.5, 129.0, 127.0, 123.8, 122.9, 122.3 ($6C_{arom}$), 115.0 (C-10), 111.7 (2CN), 21.1 (NC–**C**–CN) ppm; IR (KBr): $\nu = 2947$, 1760, 1672 cm^{-1}; UV (ethanol): $\lambda_{max} = 473$ (800), 394 (3500), 373 (4700), 355 (3800), 283 (3400), 252 (55800), 222 (17100) nm (ε). Fluorescence (ethanol): $\lambda = 380$ nm, $\Phi_f = 0.02$; MS: *m/e* (%) = 286 (M^+, 3), 256 (24), 228 (14), 193 (8), 163 (5), 149 (13), 111 (6), 94 (21), 71 (47), 57 (49), 43 (100).

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